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Recession behavior of a silicon nitride with multi-layered environmental barrier coating system

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Abstract

A silicon nitride with multi-layered environmental barrier coating (EBC) system was prepared. The multi-layered coating consisted of a thin $Lu_2Si_2O_7$ bond coat, $Lu_2Si_2O_7$/mullite eutectic intermediate layer, and a top $Lu_2Si_2O_7$ layer. A glassy phase was observed on the top $Lu_2Si_2O_7$ surface of the as-coated sample. The glassy phase was converted into $Lu_2Si_2O_7$ and Lu_2SiO_5 phases via a heat treatment at 1500 °C in Ar. The recession test was performed at 1300 °C for 500 h using high-speed steam jet equipment, which was employed to simulate the gas turbine engine conditions. Post-test examinations showed that the multi-layered EBC system well sustained during the high-temperature steam exposure test. Also, the silicon nitride substrate was protected from the oxidation and corrosion, and thus no material recession was observed. However, some cracks that run through the EBC layer was observed in the sample after the test. The substrate near the cracks oxidized, leading to the formation of a thermally grown oxide phase.

Keywords: B. Surface; C. Corrosion; D. Silicates; E. Structural applications

1. Introduction

Distributed energy (DE) resources exhibit great potential to provide more reliable energy supply than the existing electric power supply systems, and have been viewed as an important alternative or supplement to grid-connected power. The micro gas turbine is one of the systems. Because the size of micro gas turbine is small, it is difficult to improve the thermal efficiency by turbine inlet temperature (TIT). Hence, no cooling system is necessary for the development of micro gas turbine. However, when it takes into account of thermal efficiency and/or generation costs, TIT higher than 1300 °C is necessary for the development of micro gas turbine. Also, the structural components in micro gas turbines must sustain at higher than 1300 °C for long time (>30,000 h) without cooling system.

Silicon nitride ceramics have long been considered as primary candidates for the hot-section components of micro gas turbine because of their excellent mechanical properties and oxidation protection property at temperatures up to $\geq$1300 °C [1–3]. However, combustion results showed that silicon nitride ceramics exhibited substantial material recession under the gas turbine condition [4]. Several research groups carried out extensive studies to understand the recession mechanism of silicon nitride under gas turbine conditions and a model for the recession was proposed [5–7]. In general, it is believed that the surface of silicon nitride oxidizes and forms the silica scale, which is corroded by the attack of water vapor, leading to the formation of a gas state $Si(OH)_4$ specie [5–7]. The $Si(OH)_4$ gas specie is then continuously swept away by the high velocity of combustion gas, resulting in the progressive material recession.

To resolve this problem, some environmental barrier coating (EBC) systems were proposed and studied by several research groups [8–10]. In our previous reports, it was suggested that the $Lu_2Si_2O_7$/mullite eutectic bulk well sustained under static state water vapor environment and, also, $Lu_2Si_2O_7$ crystalline well

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sustained under high velocity gas combustion field, namely, actual gas turbine conditions [11].

In this paper, a silicon nitride with multi-layered EBC system was prepared and the development concept of each layer will be illustrated using our previous work. The recession test for this silicon nitride with multi-layered EBC system was conducted at 1300 °C under high-speed steam jet environment and the recession mechanism of EBC system is then discussed.

2. Experimental procedures

The SN-282 silicon nitride ceramics containing lutetium oxide (Lu_2O_3) as sintering additive (Kyocera Co. Ltd.) was used as the substrate. The multi-layer EBC consisted of a thin $Lu_2Si_2O_7$ layer bond coat, thick $Lu_2Si_2O_7$/mullite eutectic intermediate layer, and a thick $Lu_2Si_2O_7$ top layer.

The oxidation bonded by reaction sintering (OBRS) method was employed to coat the thin $Lu_2Si_2O_7$ bond coat layer on the silicon nitride substrate. By the oxidation of silicon nitride ceramics at relatively low temperatures, i.e. at below 1100 °C, a thin amorphous silica layer (~5 μm) formed on the surface via the passive oxidation. For coating of $Lu_2Si_2O_7$ layer on silicon nitride ceramics, the silicon nitride substrate with a thin layer of SiO_2 was packed with the Lu_2O_3 powder bed and sintered at 1600 °C for 4 h in argon atmosphere (0.5 MPa). The detailed procedures of the preparation of the thin $Lu_2Si_2O_7$ layer could be found in the previously published paper [1].

The deposition of the $Lu_2Si_2O_7$/mullite eutectic layer and $Lu_2Si_2O_7$ top coat layer was carried out using the plasma spray method. The mixed powders of high purity Lu_2O_3 (99.99% purity, Shin-Etsu Chemical Co. Ltd., 4 μm particle size), SiO_2 (99.99% purity, High Purity Chemicals Co. Ltd., 0.8 μm particle size), and Al_2O_3 (99.99% purity, High Purity Chemicals Co. Ltd., 0.8 μm particle size) were used for plasma spray coating. For the preparation of eutectic layer, the powder mixture with the composition of Al_2O_3:SiO_2:Lu_2O_3 = 27.3:54.6:18.1 in molar ratios [1,2] was used. For the preparation of $Lu_2Si_2O_7$ top coat layer, the powder mixture with the composition of SiO_2:Lu_2O_3 = 2.0:1.0 in stoichiometric molar ratios was used.

The recession test of the prepared sample was performed at 1300 °C for 500 h using a water injection facility at Oak Ridge National Laboratory (ORNL). The distill water was heated up to ~200 °C and directly sprayed on the sample surface via a water pump. The velocity of the steam jet was estimated to be ~50 m/s [3].

3. Results and discussions

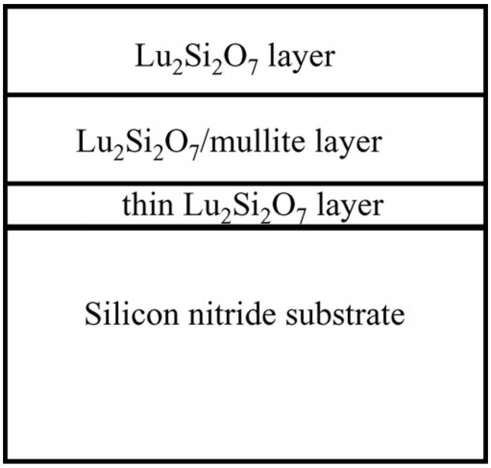

Fig. 1. The concept of multi-layered EBC system.

Fig. 1 shows the schematic for the concept of the multi-layered EBC prepared in this study. The first layer is a thin $Lu_2Si_2O_7$ layer, which is coated using the OBRS method. As shown in our previous report [1], to ensure the EBC layer adherent to the silicon nitride substrate after deposition, the coefficient of thermal expansion (CTE) of EBC employed must be close to that of silicon nitride. Thus, low CTE oxides such as rare earth di-silicates, mullite, zircon, etc. are ideal candidates for EBC materials. The materials selection tasks were conducted in our previous report, where water vapor corrosion tests were performed at 1300–1500 °C in static state water vapor environment for low CTE bulk silicates [1]. Results showed that the $Lu_2Si_2O_7$ phase exhibited the minimum material recession as compared with other oxide material evaluated. Hence, $Lu_2Si_2O_7$ phase was employed as EBC material in the present study. In addition, the corrosion rate for $Lu_2Si_2O_7$/mullite eutectic was measured to be close to zero within the experimental error.

Fig. 2 shows the X-ray diffraction pattern from the top surface of as-coated sample. X-ray result showed that both Lu_2O_3 phase and Lu-silicate containing amorphous phase were present in the as-coated sample. The center position of the broad peak indicates the amorphous phase is $2\theta = 30°$. Commonly, a broad peak for amorphous silica appears around $2\theta = 15–30°$. Hence, it is suggested that the composition of the amorphous phase shown in Fig. 2 contains Lu_2O_3 component. Consequently, a post heat treatment was performed at 1500 °C in Ar for 4 h to crystallize the top coat. Fig. 3 shows the X-ray diffraction pattern from the surface of the sample after the heat treatment. All peaks can be indexed as $Lu_2Si_2O_7$ and Lu_2SiO_5 phases, which indicated that the amorphous phase crystallized

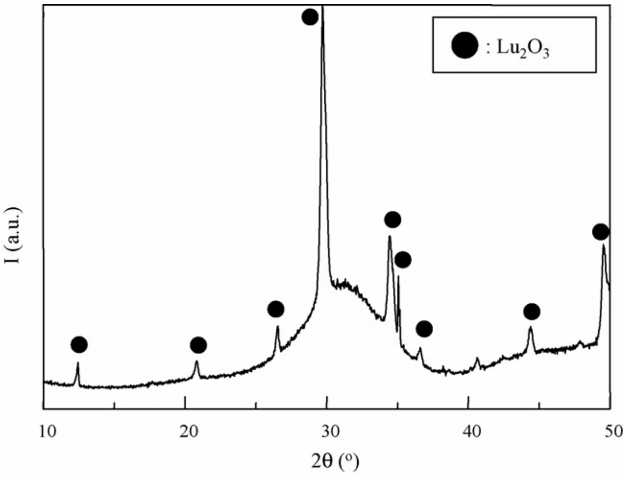

Fig. 2. The X-ray diffraction pattern from the surface of as-coated sample.

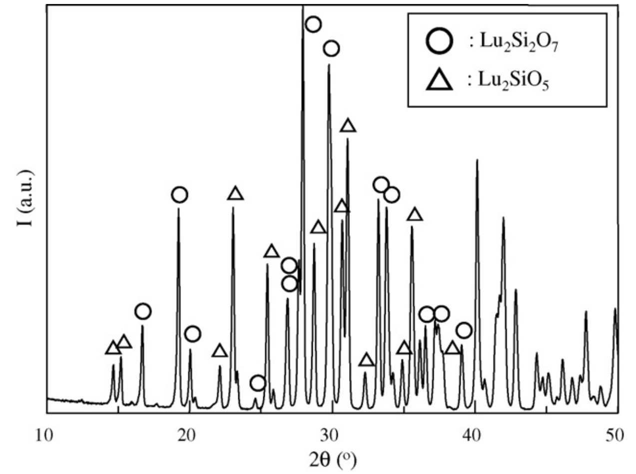

Fig. 3. The X-ray diffraction pattern from the surface of the sample after heat treatment.

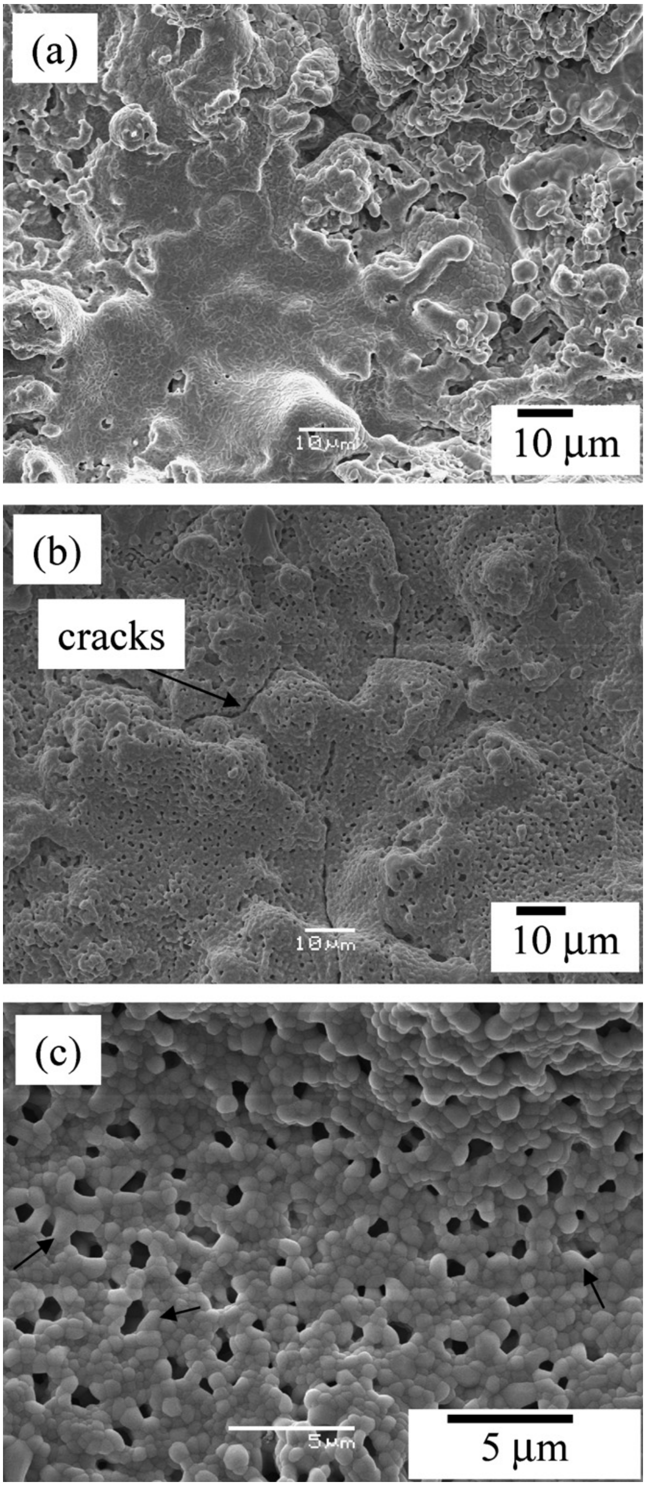

Fig. 4. SEM images of the samples surface: (a) before, (b) after the test and (c) magnified of (b).

into $Lu_2Si_2O_7$ and Lu_2SiO_5 phases during the post heat treatment. The peak intensity for Lu_2SiO_5 phase is slightly larger than that obtained from a bulk sample prepared by a hot press method from stoichiometric $SiO_2:Lu_2O_3 = 2.0:1.0$ mixed powder [4]. The difference in Lu_2SiO_5 phase peak intensity might result from a small amount of silica component that vaporized during the plasma spray process.

The recession test was performed for the heat-treated sample. In general, observations of the top surface showed that the entire coating system well sustained during the recession test. Fig. 4a and b show SEM images of the sample surface before and after the test. A porous microstructure accompanied with many cracks was observed on the coating surface after the exposure test. In the previous study [4], the recession tests for $Lu_2Si_2O_7$ bulk specimens were conducted at 1300–1500 °C in actual gas turbine conditions. A porous microstructure formed on the bulk surface due to the removal of the grain boundary silica phase. The morphology of porous microstructure observed in the present study (Fig. 4b) is very similar to the result of previous study [4]. The size of each grain is less than 1 µm, as shown in Fig. 4c. The size of grains around pores is larger than those away from pore regions. This observation suggested that grain growth occurred when the pores progressively formed during the steam exposure test. In addition, the porous microstructure could also result from the phase change of $Lu_2Si_2O_7$ to Lu_2SiO_5 due to the high temperature steam exposure as reported in previous study [4]. Note that the densities calculated from X-day diffraction data of $Lu_2Si_2O_7$ (JCPDF card data; no. 34-0509) and Lu_2SiO_5 (JCPDF card data; no. 41-0239) phases are 6.230 and 7.397 g/cm^3, respectively. Thus, the molar volume of Lu_2SiO_5 is 74.4% of that of $Lu_2Si_2O_7$. Hence, it can be hypothesized that a combination of removal of boundary phase and decomposition of $Lu_2Si_2O_7$ phase could lead to the volume reduction and thus porous structure. The progressive volume reduction resulting from the phase change could also lead to the development of residual tensile stress in affected region, resulting in crack formation observed. On the other hand, regarding to the formation of pores a liquid phase, which forms as an intermediate phase according to Eqs. (1) and (2), could be one possible mechanism for the grain growth.

$$Lu_2Si_2O_7(s) + nH_2O(g) = Lu{-}Si{-}O{\cdot}nH_2O(l) \tag{1}$$

$$Lu{-}Si{-}O{\cdot}nH_2O(l) = Lu_2Si_2O_7(s) + Si(OH)_4(g) \tag{2}$$

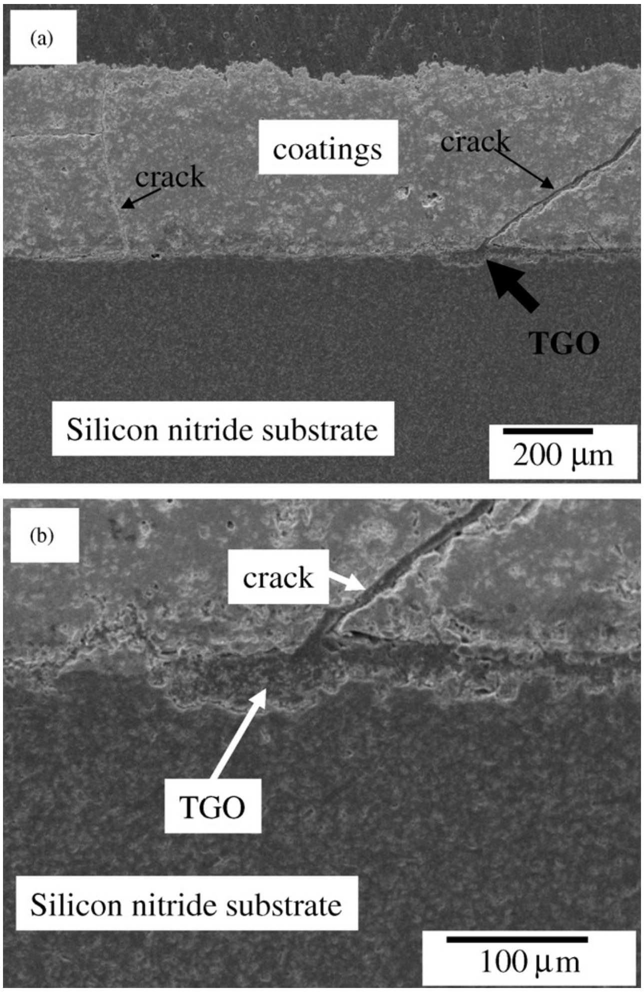

Fig. 5. Cross section images of the sample after the test.

Fig. 5a and b show the polished cross section of the multi-layered EBC sample after the test. The cracks, observed on the surface (Fig. 4b), run through the coatings. In some places, thermally grown oxide (TGO) layer was generated between substrate and coating as indicated by arrow. Silicon nitride substrate oxidized due to the inward diffusion of oxygen and/or water vapor through the cracks, consequently resulting in the formation of TGO layer. At higher magnification the TGO layer, which is very dense, can be observed only in tip region of the crack (Fig. 5b). In the oxidation and corrosion of silicon-based ceramics by water vapor, porous silica layer is commonly observed on the substrate [5]. Thus, observations suggested that the cracks and TGO layer generated were not caused by thermal shock but during the exposure test. Hence, it can be considered that the generation of cracks and TGO caused by the volume reduction of the top coat by removing boundary phase and $Lu_2Si_2O_7$ phase decomposition.

From this recession test, it was confirmed that even though a porous micro structure was formed on the top coat, the multi-layered EBC system, in general, was well sustained during the high speed steam jet exposure at 1300 °C. Nonetheless, many cracks through the coating system were generated during the test that led to the oxidation of the substrate owing to the inward diffusion of oxygen and/or water vapor.

4. Conclusions

The silicon nitride ceramics with multi-layered EBC system well sustained under high velocity steam jet environment at 1300 °C for 500 h. The surface of the top coat was corroded by water vapor. However, the multi-layered EBC system well protected the corrosion and/or oxidation of silicon nitride substrate. Some cracks that pass through the layers were induced during the test.

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